

Article

New Trends in Beverage Packaging Systems: A Review

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Abstract: New trends in beverage packaging are focusing on the structure modification of packaging materials and the development of new active and/or intelligent systems, which can interact with the product or its environment, improving the conservation of beverages, such as wine, juice or beer, customer acceptability, and food security. In this paper, the main nutritional and organoleptic degradation processes of beverages, such as oxidative degradation or changes in the aromatic profiles, which influence their color and volatile composition are summarized. Finally, the description of the current situation of beverage packaging materials and new possible, emerging strategies to overcome some of the pending issues are discussed.

Keywords: active systems; intelligent systems; packaging; shelf-life; beverages; volatile compounds; preservation; oxygen scavengers

1. Introduction

The packaging industry is conditioned by the pressures exerted by different stakeholders (producers, retailers, and consumers) who have different priorities and do not always perceive the packaging as an added value to the product [1]. The traditional functions of packaging are to protect food products from degradation processes (primarily produced by environmental factors, such as oxygen, light and moisture), to contain the food, and to provide consumers with ingredient and nutritional information [2]. These concepts have always been associated with an inert material, acting

as a “passive” barrier between the food product and the outside environment, also avoiding the migration of harmful substances from the packaging to the food [3].

Materials that have traditionally been used in food packaging include glass, metals (aluminium, foils and laminates, tinplate, and tin-free steel), paper and paperboards, and plastics. The right selection of the packaging material plays an important role in maintaining product quality and freshness during distribution and storage. Table 1 summarizes some advantages and disadvantages of different types of materials used in beverage packaging. Beverage packages often combine several materials to exploit each material’s functional or aesthetic properties. New advances in this field include the development of multilayer systems, new approaches based on active or intelligent packaging, or materials with lower environmental impacts as bio-based polymers [2,4,5].

Table 1. Some advantages and disadvantages of typical materials used in food packaging [2].

Material	Advantages	Disadvantages
Glass	Reusable and recyclable Improved break resistance allows manufacturers to use thinner glass Odorless and chemically inert Impermeable to gases and vapors Maintenance of product freshness for a long period of time without impairing taste or flavor Useful for heat sterilization Rigid Good insulation Production in numerous different shapes Variations in glass color can protect light-sensitive contents Transparent	Limitation in thin glass Heavy weight Transportation costs Brittleness Susceptibility to breakages from internal pressure, impact, or thermal shock.
Metal	Versatility Physical protection Barrier properties Formability and decorative potential Recyclable Consumer acceptance	Aluminum: high cost compared to other metals and materials (for example, steel) Inability to be welded, which renders it useful only for making seamless containers
Paper and paperboard	Lightweight Economical compared to other packaging systems Recyclable Efficient, low cost protection Available in several forms adapted to different food conditions Easy handling by consumers Very good strength to weight characteristics	Poor barrier properties to light, moisture Not used to protect foods for long periods of time When used as primary packaging, it is coated or laminated to improve functional and protective properties The combination with other materials hinders the subsequent recycling process Tears easily

Table 1. Cont.

Material	Advantages	Disadvantages
Plastic	Fluid and moldable Made into sheets, shapes, and structures Flexible Chemically resistant Inexpensive Light weight Wide range of physical and optical properties Heat sealable Easy to print Integrated into production processes where the package is formed, filled, and sealed in the same production line	Variable permeability to light, gases, vapors, and low molecular weight molecules Limited reuse and recycling properties

The use of plastics in beverage packaging has continued to increased due to the low cost of materials and functional advantages (such as thermosealability, microwavability, optical properties, and unlimited sizes and shapes) over traditional materials such as glass and tinplate [6]. In addition, plastic materials can be manufactured either as a single film or as a combination of more than one plastic by lamination or co-extrusion. Combining materials results in the additive advantage of properties from each individual material and often reduces the total amount of packaging material required. The major disadvantage of plastics is their variable permeability to light, gases, vapors, and low molecular weight molecules.

With consumers demanding higher-quality products at affordable prices and growing competition, the industrial manufacturing sector has experienced some significant changes in not only the ingredients, but also the processing and packaging systems [7]. The growing consumers' demand for minimally-processed, natural, fresh, and convenient food products, as well as continuous changes in industry caused by globalization have led to new challenges in food safety and quality. Innovations in food packaging have contributed to increasing the shelf-life of food products by the development of new packaging systems to avoid problems related to plastic-based materials, considering also the increasing legal and regulatory requirements [8]. Transmission of light and permeability to oxygen can be possible causes of food deterioration and quality loss [9]. Controlling the permeability to oxygen and moisture are major challenges to preserve the quality of food products. Indeed, the presence of oxygen facilitates the microbial growth, increases oxidative reactions, and induces the development of off-flavor and color changes [10]. For example, the variation in color produced during the storage of fruit juices can be related to the deterioration of the nutritional and organoleptic properties of the food product [11].

In response to these problems, a trend towards the development of active packaging technologies for food preservation has been promoted. Active packaging is defined as a package system designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food, and it is intended to extend the shelf-life or to maintain or improve the condition of the packaged food [12]. Therefore, this type of food packaging has the extra function of playing an active role in food preservation and quality, in addition to that of providing a protective barrier against external detrimental factors [13,14].

Some other important factors to be controlled that can affect the quality of beverage products are: pH, storage temperature, degree of interaction of volatiles with food constituents, and glass transition temperature of the polymeric material. These factors may affect the volatiles sorption capacity of food modifying the beverage composition [15].

In this review, the influence of packaging on beverage conservation and possible drawbacks for consumer acceptability are summarized. Additionally, new developments in material-based systems and current knowledge on active and intelligent packaging for beverages are reported.

2. Influence of Packaging on Beverage Conservation and Drawbacks for Consumer Acceptability

Beverage packaging can retard product deterioration, retain the beneficial effects of processing, extend shelf-life, and maintain or increase the quality and safety of food. Packaging provides protection from three major classes of external influences: (a) physical protection that shields beverages from mechanical damage and includes cushioning against the shock and vibration during distribution; (b) biological protection against microorganisms, insects, and other animals; and (c) chemical protection which minimizes compositional changes triggered by environmental influences, such as exposure to gases (typically oxygen), moisture (gain or loss), or light [2].

Traditionally, beverages have been packaged in glass containers capped with a natural or plastic cork to limit oxygen intake and preserve the organoleptic quality of the beverage. Glass offers superior barrier performance to gases and vapors, high stability over time, transparency, and it can be easily recycled [16]. However, the production and use of glass bottles have negative environmental effects due to their manufacturing energy costs; they are easily broken and are comparatively heavy (Table 1). Numerous studies based on the use of different packaging materials have been reported to overcome these problems [17,18].

The presence of molecules with low molecular weight, such as gases, water vapor, and volatile compounds, can influence or adversely affect the shelf-life of food products. Then, one of the limiting properties to be controlled in a packaged product is the sorption and transfer of these molecules through the packaging [10]. In spite of their low concentration in foods, permeation and sorption of aroma compounds on polymeric packaging materials can be detrimental to the food's organoleptic quality. As a result, significant changes in the relative presence of aroma compounds induce some alterations in the product quality and the rejection of the product by consumers [19].

The ability of the packaging to transmit oxygen and light, both involved in beverage degradation processes, should be controlled to successfully maintain the sensory and nutritional properties of food and, consequently, its shelf-life [20,21]. Degradation processes can provoke changes in color and aroma profile due to Maillard reactions which can induce the depreciation of sensory properties and the rejection of the beverage by the consumer. Moreover, the aromatic profile of the beverage can be modified by the formation of new compounds through oxidation or acid catalyzed reactions. Additionally, the vitamin C present in some beverages, such as orange juice, can be degraded by oxidative and non-oxidative pathways, which results in both nutritional and organoleptic losses [22]. All of the aforementioned reactions are related to the presence of oxygen which could be considered as the principal gas present during bottling. However, oxygen also diffuses from the surrounding atmosphere through the packaging material into the beverage with a rate depending on the

permeability of the material and the difference in oxygen partial pressure on both sides of the packaging. Therefore, appropriate barrier materials should be selected to avoid oxidative degradation, such as glass bottles, foil laminates in carton packs (e.g., Tetrapak) or flexible pouches, and polyethylene terephthalate (PET) bottles in the case of juice [17,23,24]. Bacigalupi *et al.* [20] investigated the sensitivity to oxidation of orange juice through packaging in standard or active PET with oxygen scavenger bottles. This study indicated that oxygen is a limiting parameter in the reaction of ascorbic acid degradation, being gradually consumed as it entered the package depending on its oxygen permeability properties. A large decrease in ascorbic acid content, which is the most relevant indicator of orange juice aging and quality, was obtained after 30 days of storage independent of the package [20]. Conversely, the shelf-life of orange juice packaged in monolayer PET bottles containing an oxygen scavenger, with the addition of liquid nitrogen in the headspace and an aluminum foil seal in the screw-cap, was reported to be extended by nine months at 4 °C and nearly eight months at 25 °C [22]. Wibowo *et al.* [11] indicated that color stability and shelf-life of orange juice could be extended by reducing the storage temperature and avoiding oxygen permeation through the packaging. In this study, changes in acids, sugars, oxygen, vitamin C, furfural, and 5-hydroxymethylfurfural linked to non-enzymatic browning as a function of storage time and temperature were observed [11].

In general terms, the sorption process of molecules through the packaging material can be influenced by different factors such as molecular size, polarity, solubility, and concentration of the aromatic compounds, along with the properties of the packaging material, such as morphology, glass transition, crystallinity, and polarity [25]. In the case of wine, a large number of studies have described the modification and/or evolution of oxygen, carbon dioxide, nitrogen, and sulfites inside the packaging [26]; the oxidative stability of the product [27]; the presence of aromatic compounds [15,18,28,29]; and changes in sensory, chemical [30] or physical properties [29,31]. Moreover, overall mechanisms involved after packaging such as chemical reactions (esterification, hydrolysis, and oxidation), aging, and possible transfer through the packaging or the cap that can produce any loss, increase, appearance or disappearance of aromatic compounds are reported. Esters can contribute to the fruity flavor of beverages and its evolution has a strong olfactory impact on different products. Alcohols can be degraded during storage by oxidation, involved in esterification, or formed after hydrolysis of acetates and other esters. Acids can be esterified or oxidized in shorter acids and they are formed by hydrolysis of esters, oxidation of aldehydes and reduction of alcohols during storage. Aldehydes as furfural, an off-flavor of some beverages formed by the Maillard reaction involving ascorbic acid, can appear between 3 and 5 months after packaging. Finally, lactones are cyclic molecules formed by esterification of acid and alcohol groups present in the same molecule [18,24,30,32]. Nevertheless, in addition to storage, soil and fermentation conditions, climate, and variety of grape are main factors determining the aroma of wine.

The evolution of the aromatic profile of rose wine packaged in different materials such as glass, virgin and recycled PET bottles was studied by Dombre *et al.* [10,33]. The appearance of new compounds (furfural derivatives, 5-hydroxymethyl furfural, and ethyl pyruvate or dioxanes) independently of the packaging type was observed. However, the appearance of specific compounds from the packaging as diethyl tartrate in glass, ethyl pyruvate in virgin and recycled PET, and vanillin in virgin PET was also observed [18]. Revi *et al.* studied the effect of the packaging material on some

enological parameters of dry white wine. Parameters monitored included titratable and volatile acidity; pH; total and free SO₂ content; color; volatile compounds and sensory attributes. Dark-colored glass and two commercial bag-in-box (BIB) pouches (LDPE and ethylene vinyl acetate-EVA lined) were used as packaging materials. The BIB materials affected the titratable acidity, total and free SO₂ and color of wine. A substantial portion of the wine aromatic compounds was adsorbed by the plastic materials or lost to the environment. Sensory evaluation showed that white wine packaged in both plastics was of acceptable quality for three months vs. at least six months for that in glass bottles [15].

The sorption of 14 aromatic compounds into PET and polyvinyl chloride (PVC) during the storage of strawberry syrup for one year was studied by Ducruet *et al.* [34]. The amount of absorbed aroma was four times higher in PVC than in PET, but less than 0.1% of the initial amount present into the syrup. As a result, interactions between aromatic compounds and packaging may result in a dynamic and time-dependent change in food quality during shelf-life. Two combined mechanisms contributed to the loss of aroma during long-term storage: the degradation process in the food product itself and the sorption process in the packaging material [34].

Additional studies are necessary to help food industry to understand and predict the behavior of aromatic compounds, especially those sensitive to degradation during long-term storage, taking into account both the effects of the food matrix and the packaging.

3. New Emerging Strategies

3.1. Material/Structural Modifications

Glass and metals provide a nearly absolute barrier to chemical and other environmental agents. The effect of different packaging materials (galvanized tin, polythene, colorless, brown and black glass containers) on the physicochemical properties of sunflower oil was evaluated by Abdellah *et al.* [35] to minimize oil deterioration and prolong its shelf-life. The obtained results showed that the glass container seemed to be more resistant to deterioration factors than polythene while galvanized container was found to be the worst. Regarding glass bottles, the brown container revealed more resistance to oxidative stability followed by colorless and black containers. Brown color may act as a protective shelter from light, since light is incriminated in the breakdown of pigments and vitamins present in vegetable oils. Relative degradation of an oil sample stored in a black container may be attributed to temperature absorbed by black color, as temperature plays an important role in the breakdown of oils and fats to fatty acids and glycerol. In general, glass containers are described to be the best packaging material for edible oils storage [35].

Plastic packaging offers a large range of barrier properties but is generally more permeable than glass or metal. The shelf-life of perishable products can be increased by using packaging materials that could control or minimize the permeation of different gases towards the internal atmosphere. Barrier properties are mainly correlated to the intrinsic structure of the polymer such as the degree of crystallinity; nature of the polymer; crystalline/amorphous phase ratio; mechanical and thermal treatments; polarity of chemical groups present into the polymer; degree of crosslinking; and glass transition temperature [36]. These properties also depend on external conditions, such as temperature and differences in pressure and relative humidity.

New trends in the area of food packaging have been focusing on the development of new materials with enhanced properties to control food-package-environment interactions. In the case of glass containers, surface treatments are very promising for improving the hydrolytic resistance of the glass surface. Naknikham *et al.* [37] studied different surface treatments based on rinsing the glass on several solutions, then cleaning and drying at 110 °C for 20 min. Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), citric acid, ammonium sulfate and acetic acid were used as surface modifiers. Satisfactory results were obtained by treating the glass with 5 wt% alum showing an increase in the hydrolytic resistance [37]. Regarding plastic materials, PET is increasingly used in beverage packaging for liquids such as milk or oil due to its excellent mechanical properties, clarity, UV resistance, and good oxygen barrier properties. Moreover, these properties can be improved by combining different films (multilayer PET) or by adding oxygen scavengers which act by reducing the oxygen content dissolved in the beverage and present in the headspace but also by limiting oxygen ingress and increasing the shelf-life [20]. Figure 1 shows a scheme for the general mechanism of gas or vapor permeation through a multilayer beverage packaging system including an oxygen scavenger.

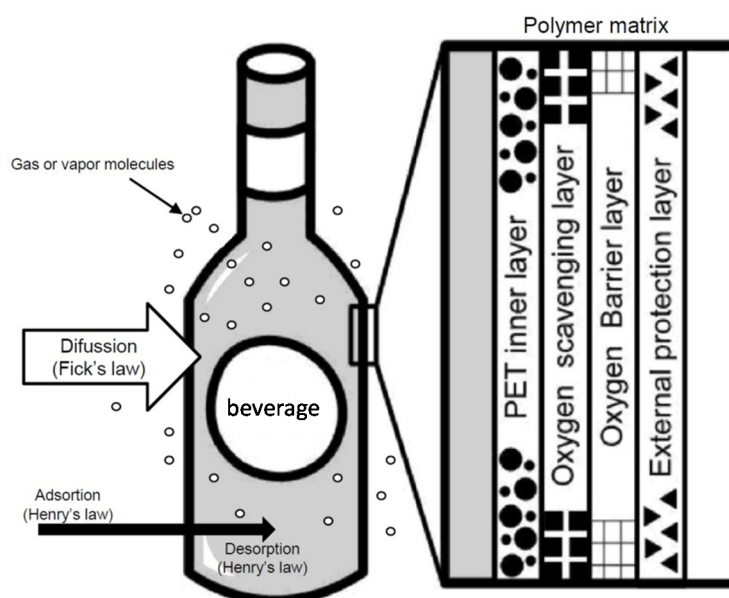


Figure 1. Scheme for the general mechanism of gas permeation through a multilayer beverage packaging system including an oxygen scavenger.

The influence of PET-based packaging systems on the quality of orange juice has been already reported. Ros-Chumillas *et al.* [22] studied different packaging systems (glass, multilayer and monolayer PET bottles) showing monolayer PET the lowest retention of ascorbic acid during storage and shelf-life compared to multilayer PET and glass. Oxygen was the main factor contributing to ascorbic acid degradation which was linked to differences in the materials oxygen permeability. The obtained results indicated that glass was the material presenting the lowest oxygen permeability followed by multilayer and monolayer PET [22]. Berlinet *et al.* [17] studied new multilayer PET systems with decreased oxygen permeability to maintain the quality of orange juice. Three different PET-based packaging materials were used: standard monolayer, multilayer, and plasma-treated (internal carbon coating). Compared to standard PET, multilayer or internal carbon coating PETs with

good oxygen barrier properties were obtained showing better vitamin C contents after three months of storage. Flavor compounds as well as vitamin C play a major role on maintaining the quality of orange juice [17].

Innovations in the packaging industry have led to the development of novel sustainable materials as an alternative to the classic packaging systems. Starch-based packaging materials have attracted much interest because of its biodegradability to ease the environmental crisis and the petroleum shortage arising from the consumption of traditional polymers. Huang *et al.* studied the relationship between structural changes and plasticizer migration of starch-based films for milk packaging during microwave heating, concluding that this novel hydrophobic food packaging material could open doors to new opportunities for beverage packaging applications [38].

3.2. Active and Intelligent Systems

The packaging industry has been focusing on the development of solutions to provide maximum food security while maintaining the nutritional value at competitive prices. As a result, food packaging products have evolved from simple preservation containers to include aspects such as convenience, point of purchase, marketing issues, material reduction, safety, and environmental-friendly materials [8]. In this context, new technologies are being investigated in this wide research field, such as smart packaging and active packaging systems [39].

Some reports, such as “*Global Active, Smart and Intelligent Packaging Market By Products, Applications, Trends and Forecasts (2010-2015)*” [40], analyze the active and smart packaging market by classifying by technology and applications; while studying the major market drivers, restraints and opportunities for these technologies in North America, Europe and Asia. According to this source, the active packaging technologies held the highest growth rate in 2010 being estimated for a 10.5% increase from 2010 to 2015. Modified atmosphere accounted for the largest share (approximately 54%) of the total market in advanced packaging technology. Out of the total market for the global advanced packaging, the contribution of food sector is 51%, while this is reduced to 19% for beverages. “Active food packaging” is a good example of an innovation that goes beyond the traditional functions of packaging materials in which the package, the product and its environment interact to extend the food shelf-life and/or to improve its safety or sensory properties; while maintaining food quality. Antimicrobials, antioxidants, and controllers of moisture, odor, and gases are usually added as active agents. Conversely, “intelligent food packaging” only provides information to the processor, retailer and/or consumer of the status of the food or its surrounding environment. Anti-theft indicators, locating devices, and time-temperature sensors are usually used [41]. In the present section, recent trends in active and intelligent beverage packaging are summarized.

3.2.1. Active Systems

Active food packaging is a heterogeneous concept involving a wide range of possibilities which globally can be classified in two main groups [8]: (a) active packaging to extend the shelf-life which allows controlling the mechanisms of deterioration inside the package by using different systems, such as oxygen scavengers, moisture absorbers or antimicrobial and antioxidant agents, and (b) active packaging to facilitate processing and consumption, which allows matching the package to the

properties of the food, reducing processing costs, or even performing some processing operations in-package or controlling the product history and quality. So, the novelty associated with this type of packaging is based on the purpose not only to diminish the deterioration of food within the package, but also to induce positive changes during the shelf-life of the packaged product, reducing the need of direct addition of chemicals and/or releasing agents to food under controlled conditions.

Table 2. Recent trends in active beverage packaging.

Active packaging	Application	Principle	Material	Reference
Antioxidant	Fruit juices	Release of encapsulated antioxidants	Plastic	[13]
	Beer	Oxygen scavenger crowns	Metal	[42]
	Orange juice	Oxygen scavenger films	Plastic	[21]
	Aqueous food products	Oxygen scavenger films	Plastic	[43]
	Beer and wine	Glucose oxidase and catalase oxygen scavengers	Metal and glass	[44]
	Wine, beer, flavoured alcoholic beverages and malt-based drinks	Polymeric oxygen scavenging system (PET/nylon/cobalt)	Plastic	[45]
	Beer	Oxygen consumption by immobilized yeast in sealed packaged	Metal	[46]
	Beverage bottles	Viable spores as oxygen scavengers into PET copolymer	Plastic	[47]
Antimicrobial	Raw and pasteurized milk, yogurt and fermented dairy beverages	Carbon dioxide addition at elevated pressure	Plastic	[48]
	Orange juice and liquid egg white	Nisin bacteriocin as polymer coating	Plastic	[49]
	Water, cantaloupe juice and pineapple juice	Vanillin addition as natural antimicrobial agent into natural polymer films	Plastic	[20]
	Apple and orange juices	Silver or ZnO nanoparticles	Plastic	[50]
	Melon and pineapple juices	Cellulose/copper antimicrobial composites	Plastic	[51]
	Apple juice	Silver nanoparticles	Plastic	[52]
	Kiwi and melon juices	Cellulose/silver nanocomposites	Plastic	[53]
Functional	UHT milk	Lactase-active or cholesterol-active package	Plastic, metal and glass	[54]
	Beer	Gas emission		
	Milk, drinks and water	Flavor release		
	Health, wellness, and sport drinks	Nutrient release		
	Drinkable yogurt	Probiotic release		
	Orange juice and wine	Odor removal		
Self-heating	Chocolate, soup and coffee	Glycerol and potassium salt reaction	Plastic	[55]
Self-cooling	Beer and soft drinks	Water and desiccant reaction	Plastic and metal	[56]

Table 2 summarizes the main applications of active packaging mainly used for beverage preservation, enhancing their organoleptic quality in flavor, taste, and color. In general, recent trends in active packaging for beverages have been focused on the development of two types of systems: (a) packaging systems (mainly plastics and metallic materials such as bottles and cans) with scavenging agents incorporated into the closure (crown), and (b) new active plastic materials (mainly

natural or synthetic plastic films). New advances in plastic packaging have led to the development of natural polymers-based systems which show several advantages such as biodegradability, environmental friendliness, low cost, high efficiency as active supports, and similar processing conditions to synthetic polymers.

Oxidation and microbial growth are the main quality-deteriorating factors of beverages [42]. Regarding antioxidant packaging, antioxidant compounds are usually used as active agents in packaging processing; that is, the active agent is incorporated into the walls of the material exerting its action by absorbing undesirable compounds from the headspace or by releasing antioxidants to the food or the headspace surrounding it [13]. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are the most widely used synthetic antioxidants for preventing oxidation in food products [57]. However, the use of such compounds in food packaging formulations is currently under discussion due to toxicological concerns. As a result, there is a growing interest in the use of natural antioxidants in active food packaging, not only by their perceived harmless character to humans but also by their good performance in limiting oxidation processes in the material and/or food, as well as the good acceptance by consumers of the use of natural additives. The alternative of using natural antioxidants, particularly tocopherols, of plant extracts and essential oils from herbs and spices, and also from agricultural waste products, is being currently evaluated. Many different natural extracts have been incorporated into biodegradable materials in order to achieve antioxidant properties [58,59].

Nowadays, new antioxidant packaging materials are being continuously developed for the manufacture of beverage packages, by applying the latest advances in microencapsulation, biotechnology and packaging technologies. As an example, a new packaging for fruit juices with biodegradable and antioxidant properties (to extend the life of the beverage product) made from sugars and other residues rich in carbon, nitrogen, and oxygen present in the waste water from juice bottling industries is being developed under the project PHBOTTLE [60].

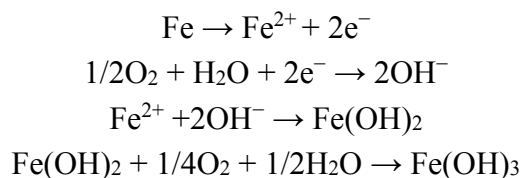
Many foods are very sensitive to oxygen, which is responsible for the deterioration of many products either directly or indirectly [61]. The presence of oxygen into the package increases beverage deterioration mainly due to aerobic microbial and molds growth, enhancing oxidative reactions that lead to color changes, off-odors, and flavors development and reducing nutritional quality [62]. The use of oxygen scavengers has been extensively studied and applied by many researchers and companies. Oxygen-absorbing technology is based on oxidation or combination of components such as iron powder, ascorbic acid, photosensitive polymers, enzymes, *etc.* These compounds are able to reduce the levels of oxygen to below 0.01%, which is lower than the levels typically found (0.3%–3%) in the conventional systems of modified atmosphere, vacuum or substitution of internal atmosphere for inert gas. A variety of oxygen scavenging systems has been developed to match the requirements of different beverage products (Table 2).

Oxygen-scavenging packaging has been widely applied in the preservation of beer by the incorporation of scavenging agents into the closure (crown) by two methods: (a) into a sachet inside of the closure with a membrane to separate the scavenger from the beer; or (b) incorporated into a polymer coating on the inside of the closure [42]. Ascorbic acid is an oxygen scavenger component which action based on ascorbate oxidation to dehydroascorbic acid. This reaction can be accelerated by light or a transition metal which will work as catalyst, e.g., copper. The ascorbic acid reduce the

Cu^{2+} to Cu to form the dehydroascorbic acid. The cuprous ions (Cu^+) form a complex with the O_2 originating the cupric ion (Cu^{2+}) and the superoxide anionic radical. In the presence of copper, the radical leads to the formation of O_2 and H_2O_2 . The copper-ascorbate complex quickly reduces the H_2O_2 to H_2O without the OH^- formation, a highly-reactive oxidant. The total capacity of the O_2 absorption is determined by the amount of ascorbic acid. The complete reducing of 1 mol of O_2 requires 2 moles of ascorbic acid [63]. Crowns with copper and iron metals combined with ascorbate salts have been found to reduce oxygen levels in beer bottles after 1–3 months of storage maintaining the effect to 12 months [42]. The evaluation of ascorbic acid loss due to the presence of oxygen in orange juice packed in oxygen scavenging and oxygen barrier films was also carried out. As a result, ascorbic acid was maintained over long storage times as a consequence of the rapid removal of oxygen [21]. Ascorbic acid and ascorbate salts are being used in the design of scavengers in both sachet and film technologies. The active film may contain a catalyst, commonly a transition metal (Cu, Co), and it is activated by water, being that this technology is especially indicated for aqueous food products [43].

Other oxygen scavengers have been developed with the combination of two enzymes, glucose oxidase and catalase, that would react with some substrate to scavenge incoming oxygen being part of the packaging structure or put in an independent sachet. The glucose oxidase transfers two hydrogens from the $-\text{CHOH}$ group of glucose, that can be originally present or added to the product, to O_2 with the formation of glucono- δ -lactone and H_2O_2 . The lactone then spontaneously reacts with water to form gluconic acid. This system has been used in beer and wine bottles [43].

Another scavenging technology is based on the principle of iron oxidation in water presence. The action mechanism of this type of oxygen scavenger is very complicated and it is described by the following reactions [63]:



The commercial oxygen scavengers available are in form of small sachets containing metallic reducing agents, such as powder iron oxide, ferrous carbonate, and metallic platinum. A self-reacting type contains moisture in the sachet and as soon as the sachet is exposed to air, the reaction starts. In moisture-dependent types, oxygen scavenging takes place only after moisture has been taken up from the food. Some important iron-based O_2 absorbent sachets are Ageless[®] (Mitsubishi Gas Chemical Co., Japan), ATCO[®] O_2 scavenger (Standa Industrie, France), Freshlizer[®] Series (Toppan Printing Co., Japan), Vitalon (Toagosei Chem. Industry Co., Japan), Sanso-cut (Finetec Co., Japan), Seaquil (Nippon Soda Co., Japan), FreshPax[®] (Multisorb technologies Inc., USA), and O-Buster[®] (Dessicare Ltd., USA).

An alternative to the use of sachets is the integration of the scavenger directly into the polymeric film structure. Scavengers can be dispersed in the polymer matrix or introduced as an inner layer in a multi-layered film, including the sidewall or lid of rigid containers, flexible films and closure liners. The speed and capacity of these scavenging films are considerably lower than iron-based scavenger sachets, but they are more acceptable and safer by consumers [64–66]. Mahieu *et al.* [67] developed a binary oxygen scavenger, composed of ascorbic acid (AA) and iron powder (Fe) as catalyst, added in

extruded thermoplastic starch (TPS) films. The obtained TPS-AA-Fe films showed interesting oxygen-scavenging properties which can be triggered by an increase of water content in the film. As a result, this material could be of interest for the development of short life-time active food packaging [67]. Oxyguard® (Tokyo Seikan, Japan), Shelfplus O₂® (Albis Plastic GmbH, Hamburg, Germany) or Ageless Omac® (Mitsubishi Gas Chemical America, Inc., New York, USA) are some examples of iron-based oxygen scavengers in beverage products. Shelfplus O₂® is well-incorporated into the packaging material (PP or LDPE), which acts as an absorber of the oxygen left in the packaging headspace and in the product itself providing a greatly improved barrier and optimum protection [68]. Finally, novel potential oxygen scavengers based on iron containing kaolinite [66] or iron nanoparticles [69] have been evaluated for broad application as active packaging systems in a variety of oxygen-sensitive foods, increasing the reaction activity of iron powder and then the oxygen absorption capacity of oxygen scavengers.

During storage, some undesirable by-products such as organic acids, aldehydes or ketones can be produced affecting the quality of the product. As a solution, adsorber materials have been developed in the last decades. For example, Oxbar™ is a system developed by Carnaud-Metal Box (Shipley, West Yorkshire, UK) which involves cobalt-catalyzed oxidation of a nylon polymer blended in PET bottles for packaging of wine, beer, sauces, flavored alcoholic beverages, and malt-based drinks [45]. Conversely, the use of yeast to remove oxygen from the headspace of hermetically-sealed beer packages has been patented. The yeast is activated and respire inside the bottle, consuming oxygen and producing carbon dioxide plus alcohol [46].

Other alternative oxygen scavenging systems have been also reported. Anthierens *et al.* [47] developed an oxygen scavenger using an endospore-forming bacteria genus *Bacillus amyloliquefaciens* as the “active ingredient”. Spores were incorporated in poly(ethylene terephthalate, 1,4-cyclohexane dimethanol) (PETG), an amorphous PET copolymer having a considerable lower processing temperature and higher moisture absorption compared to PET. The use of viable spores as oxygen scavengers could have advantages towards consumer perception, recyclability, safety, material compatibility and production costs compared to currently available chemical oxygen scavengers [47].

Antimicrobials in beverage packaging are used to enhance quality and safety by reducing surface contamination of processed food, reducing the growth rate and maximum population of microorganisms by extending the lag phase of microbes or inactivating them [62]. The development of antimicrobial packaging materials has been raised in last years for its use in beverage packaging, studying antimicrobial agents such as silver ions, nisin, organic acids, spice-based essential oils, and metal oxides, among others (Table 2). Carbon dioxide has been added to milk, yogurt, and fermented dairy beverages as an antimicrobial agent for shelf-life extension [48]. Nisin is a heat-stable bacteriocin produced by certain strains of *Lactococcus lactis* and it is primarily active against Gram-positive bacteria, including *Clostridium*, *Bacillus*, *Staphylococcus* and *Listeria* species. A variety of polymer films have been used to deliver nisin to beverages. Jin and Zhan developed polylactic acid (PLA)/nisin films which could be used to make bottles or be coated on the bottle surface for their use in liquid food packaging, such as orange juice or liquid egg white, to avoid the microorganisms proliferation [49]. Additionally, the diffusion kinetics and factors affecting the

migration of vanillin from chitosan/methyl cellulose films into water, cantaloupe juice, and pineapple juice were reported with an inhibitory effect against different microorganisms [70].

Metallic-based micro- and nanostructured materials are incorporated into food contact polymers to enhance mechanical and barrier properties and to prevent the photodegradation of plastics. In addition, heavy metals are effective antimicrobials for food preservation purposes in the form of salts, oxides, and colloids, complexes such as silver zeolites, or as elemental nanoparticles [71]. Nanomaterials and nanoparticles may include any of the following nano forms: nanoparticles, nanotubes, fullerenes, nanofibres, nanowhiskers, nanosheets. Silver based nano-engineered materials are currently the most commonly used in commodities due to their antimicrobial capacity. Copper, zinc, and titanium nanostructures are also showing promise in food safety and technology. Recent developments in nanotechnology to enhance the storability of fruit juices have been reported by the addition of Ag and ZnO nanoparticles as antimicrobial agents [50]. Copper is commonly applied in food safety in the form of copper salts due to its antibacterial and antifungal properties. Sub-lethal concentrations of copper (50 mg kg^{-1}), in the form of copper sulfate pentahydrate, have been reported to stop the growth of *Salmonella*, *Escherichia coli* O157:H7, and *Cronobacter* if combined with lactic acid in infant formula [72] and carrot juice [73]. The antimicrobial activity of copper oxide composites was evaluated in contact with melon and pineapple juices obtaining an excellent antifungal activity by reducing about 4 Log cycles the loads of spoilage-related yeasts and molds [51]. Del Nobile *et al.* tested the antimicrobial activity of plasma deposited silver clusters against *Alicyclobacillus acidoterrestris* and found encouraging results in a food simulant and apple juice [52]. In addition, total viable microorganisms, yeasts, and molds were reduced up to 99.9% in kiwi and melon juices in contact with cellulose/silver nanocomposites confirming the antimicrobial activity of silver nanoparticles [53]. However, prior to industrial implementation, regulations need to be considering the potential risks associated to the nano-dimension and the potential migration of metal ions into drinks.

Functional food packaging has been increasing its importance in the beverage industry as a technology for fast moving consumer goods [54]. Some examples are gas release in beer; flavor-releasing packaging (chocolate-flavored, bottled water and milk-based drinks); nutrients release in health, wellness and sport drinks; and probiotics release into drinkable yoghurt. Flavor scalping, or permeation of aromatic components, may result in loss of flavor and taste intensities and/or changes in the organoleptic profile of beverage products. For example, the bitter principle, limonin, builds up in orange juice after pasteurization and renders juice from some cultivars undrinkable. The substantial quantities of limonin could be removed by acetylated paper, involving cellulose acetate gel beads. In addition, some immobilized enzymes that were initially applied in food production lines are currently being considered for food packaging applications. For instance, UHT milk can be packaged in a lactase-active or cholesterol-active package, obtaining, through storage, a low/free-lactose or low-cholesterol product, respectively. Sulfites have also been proposed as active substances for their use in plastic gasket liners of wine.

Finally, self-heating packages, for chocolate, soup and coffee, and self-cooling containers for beer and soft drinks have been under active development for more than a decade, but they have yet to achieve commercial status [74]. Self-heating technology is based on the reaction between glycerol and potassium salt. In these systems, it is necessary to tailor the heat generation to control the rate at which

the reaction occurs, to introduce a lag before the reaction initiates, and to control the ultimate temperature reached by the product. Regarding self-cooling systems, Crown Cork and Seal (CROWN Packaging Europe GmbH, Baarermatte, Switzerland) [55] is a pioneering company on the development of a self-chilling beverage can in conjunction with Tempra Technologies (Florida, EE.UU) [56] by using the latent heat of evaporating water to produce the cooling effect. The water is bound in a gel layer coating a separate container within the beverage can, and it is in close thermal contact with the beverage. To activate the system, the consumer twists the base of the can to open a valve which exposes the water to the desiccant held in a separate evacuated external chamber. This initiates evaporation of the water at room temperature and, thus, achieves a cooling effect as the heat is removed from the system.

3.2.2. Intelligent Systems

Nowadays, three major technologies exist for realizing intelligent packaging of beverages [75]: (a) sensors, (b) indicators, and (c) radio frequency identification (RFID) systems (Table 3).

A sensor is defined as a device used to detect, locate or quantify energy or matter, giving a signal for the detection or measurement of a physical or chemical property to which the device responds [54]. In general, printed electronics, carbon nanotechnology, silicon photonics, and biotechnology have been used as potential sensors in different food matrices such as meat, fish, ready-to-eat products, among others [75]. Sensors have been considered as the most promising and game-changing technology for future intelligent packaging systems.

Recent research in the field of intelligent packaging materials for beverages have led to the development of nanosensors and nanomaterials for the detection of food-relevant analytes such as small molecular contaminants, food-borne pathogens, allergens or adulterants in complex food matrices [76]. Nanosensors can be classified into three main types: nanoparticle based sensors, optical nanosensors and electrochemical nanosensors. Many of the assays used in nanosensors are based on observed color changes that occur to metal nanoparticle solutions in the presence of analytes. For example, gold nanoparticles (AuNPs) and crown-ether-modified thiols were used to determine melamine content, an adulterant, in raw milk and infant formula. The melamine bonded into the surface of AuNPs produce a color change from red to blue. This method enables on-site and real-time detection of melamine without the aid of any advanced instrument [77]. Another efficiently fluorescence-based assay was reported to detect cyanide in drinking water using fluorescence quenching of gold nanoclusters [78]. A nanoscale liposome-based fluorescence detector for the determination of contamination in drinking water with pesticides was also devised by Vamvakaki *et al.* [79]. Nanoscale magnetic particles were used to isolate *Mycobacterium avium* spp. *paratuberculosis* from contaminated whole milk to determine the bacterial concentration by observing effects of conjugation-induced magnetic particle agglomeration on the spin-spin relaxation times of nearby water protons [80].

Table 3. Recent trends in intelligent beverage packaging.

Intelligent Packaging	System	Application	Principle	Packaging Material	Reference
Sensors	Optical	Milk	Melamine content by colorimetric method	-	[77]
	Optical	Water	Cyanide content by fluorimetric method	-	[78]
	Optical	Water	Pesticides detection by fluorimetric method	-	[79]
	Electrochemical	Commercial beverages	Glucose content	-	[81]
	Electrochemical	Milk	Aflatoxin-B17 content	-	[82]
	Magnetic nanomaterial	Milk	<i>Mycobacterium avium</i> spp. <i>Paratuberculosis</i> concentration	-	[80]
	Carbon nanotubes	Water	Cyanobacteria toxin content	Porous fibrous materials: fabrics and papers	[83]
Indicators	Gas indicator	Water, oil and beverages	Oxygen indicator	Plastic	[84]
		Liquid products	Gas escape from packaging	Plastic	[85]
			Polymerization color reaction	Plastic	[86]
	Time temperature indicator	Milk	Enzymatic hydrolysis of a lipid substrate with pH reduction	Plastic and carton	[87]
		Wine	Thermosensitive compounds and color change reaction	Glass	[88]
	Thermochromic ink	Beer	Temperature sensor	Metal and glass	[89]
		Orange juice	Temperature sensor	Plastic and glass	[90]
		Coffee	Temperature sensor	Plastic	[91]
	Freshness indicator	Coffee	Time detector related to freshness settings	Plastic	[92]
	RFID (radio frequency identification)	Fat-free and whole milk	Monitor milk freshness	Carton	[93]
		Wine	Monitor temperature	Glass	[94]
		Water	Monitor temperature	Plastic	[95]
		Liquors	Anti-counterfeiting, logistics and evidence that duty has been paid	Glass	[96,97]

Electrochemical nanosensors operate by binding selective antibodies to a conductive nanomaterial and then monitoring changes to the material's conductivity when the target analyte binds to the antibody. Compared to optical methods (colorimetric or fluorimetric, electrochemical detection may be

more useful for food matrices because the problem of light scattering and absorption from the various food components can be avoided [76]. AuNPs and glucose-sensitive enzymes can be used to measure glucose concentrations in commercial beverages [81]. A reusable piezoelectric AuNP immunosensor has been also developed to detect the presence of aflatoxin-B17 in contaminated milk samples [82]. In addition, conduction changes which occur when Microcystin-LR, a toxin produced by cyanobacteria, binds to the surface of anti-MCLR-coated single-walled carbon nanotubes are easily detectable in drinking water [83].

Optical techniques are more commonly employed for pathogen detections and they are based on fluorescence and Surface Plasmon Resonance (SPR). These techniques generally rely on monitoring the change of the optical signal that occurs between a functionalized nanomaterial and a pathogen. This type of sensors can be introduced into the deeper part of cells with minimal physical perturbation of the cell. Nanomaterials, such as AuNPs, gold nanorods (NRs), Fe₃O₄NPs, and quantum dots (QDs) have very good optical properties which make them excellent optical labels for improving the sensitivity of optical transducer surfaces of nanosensors. Optical transducers are particularly attractive for developing robust devices, easy to use, portables and, if possible, with an inexpensive analytical system [93].

In the last years, there has been an exponential increase in the use of nanomaterials for sensing purposes as a result of the increasing need for simple, small, selective, and reversible chemical sensors with low limits of detection and operating temperatures in a wide spectrum of applications. In particular, carbon nanomaterials (CNs), such as nanoparticles (carbon black and fullerenes), graphene, graphite (*i.e.*, stacked graphene) nanofibers, and nanotubes have been attracting a great interest. These materials offer a high specific surface area, and excellent detection sensitivity, electrical properties, and mechanical characteristics [75]. As a result, these materials show a great potential to be applied in chemical sensors.

Indicators provide immediate visual information about the packaged food by means of a color change, an increase in color intensity or diffusion of a dye along a straight path, which might be irreversible for not causing possible false information. In contrast to sensors, indicators cannot provide information about a quantity and cannot store the data of measurement and time. Gas sensors, time-temperature devices, thermochromic inks, and freshness indicators have been mainly developed in the last few years. Gas sensors are devices that respond reversely and quantitatively to the presence of a gaseous analyte by changing the physical parameters of the sensor, and they are monitored by an external device [54]. For example, the OxyDot[®] (Oxy Sense Inc., Las Vegas, EE.UU.) is a non-invasive, light sensitive, oxygen sensor which is placed inside a bottle or package prior to filling and sealing. The measurements are achieved with a fiber-optic reader pen from outside the package [84]. In this system, the oxygen measurement technique is based upon the fluorescence quenching of a metal organic fluorescent dye immobilized in a gas permeable hydrophobic polymer. The dye absorbs light in the blue region and fluoresces within the red region of the spectrum. The presence of oxygen quenches the fluorescent light from the dye as well as its lifetime. Similarly, the UPM label “Shelf Life Guard” turns from transparent to blue, informing the consumer that air has replaced the modified atmosphere gases within the package [85].

A time-temperature indicator (TTI) is a simple, inexpensive device that shows an easily measurable time-temperature dependent change that reflects the full or partial temperature history and quality status of the food product to which it is attached [98]. In this way, these indicators react to time and temperature in the same way that a food product does, giving a signal about the state of freshness and remaining shelf-life. Some commercial indicators can be found for milk products, such as Fresh-Check® (Temptime Corp., Morris Plains, NJ, USA) [86] which is based on a solid-state polymerization reaction, resulting in a highly-colored polymer. Similarly, the CheckPoint® (VITSAB A. B., Malmö, Sweden) is a simple adhesive label based on enzymatic system. This label is based on a color change caused by a pH decrease that is the result of a controlled enzymatic hydrolysis of a lipid substrate [87]. Regarding wine, excessively high temperatures for several hours will have a detrimental effect on its chemistry with the production of off-flavors resulting from oxidation and other undesirable reactions. In this context, the OnVu™ (Ciba Specialty Chemicals and Freshpoint, Switzerland) [88] is a newly introduced solid state reaction TTI which is based on photosensitive compounds that change color with time at rates determined by temperature.

Thermochromic inks are dyes that react in reference to temperature and not in a chemical nature. This technology is used in the beverage industry to display a readiness for consumption. An example of such is the Coors Light® branded bottle, where a thermochromic ink is used to symbolize that the beverage has reached the desired temperature for consumption [89]. Other example is the color changing coffee cup lid from Smart Lid Systems™ (Sydney, Australia) [91]. The smart lid is infused with a color changing additive which allows it to change from a coffee bean brown to a bright red color when exposed to an increase in temperature. If the red color is too intense, it indicates to consumers that the coffee in the cup is too hot for comfortable drinking. Similar examples can be found on supermarket shelves for orange juice pack labels incorporating thermochromic-based designs to inform the consumer when a refrigerated orange juice is cold enough to drink [90]. This technology has been integrated also in beverage machinery. In this context, the Curtis ALP3GT™ Brewing Systems with FreshTrac™ technology [92] is a revolutionary way to keep decanters ready to serve freshly brewed coffee. FreshTrac™ includes a visual indicator to monitor the freshness of coffee which can range from 10 to 120 min.

Finally, radio frequency identification (RFID) technology does not quite fall into either sensor or indicator classification but rather represents a separate electronic information based form of intelligent packaging. RFID systems contain a chip, an antenna, and an external host system that can power the device allowing information to be transferred to the reader. The reader (a read/write device composed of a transmitter and/or a receiver) uses electromagnetic (EM) waves to communicate with an RFID tag through the antennas. These systems are typically used for identification, automatization, antitheft prevention or counterfeit protection. The tags can contain a variety of information, such as location, product name, product code and expiration dates [99].

According to Vanderoost *et al.* [75], RFID tags may be classified into three types on the basis of power supply: passive, semi-passive, and active. Passive RFID tags have no battery and are powered by the EM waves emitted by the reader. Semi-passive tags use a battery to maintain memory in the tag or power the electronics that enable the tag to modulate the EM waves emitted by the reader antenna. Finally, active tags are powered by an internal battery, used to run the microchip's circuitry and to

broadcast a signal to the reader. Active tags generally ensure a longer read range than passive tags, but are more expensive than the latter. Potyrailo *et al.* reported the use of passive RFID sensors for monitoring the freshness of milk [93] which were constructed using 23×38 mm RFID tags from Texas Instruments (Plano, TX, USA). Changes in the dielectric properties of milk were sensed with these RFID sensors that had an adhesive backing attached to the side wall of the milk cartons. RFID tags can be also used to help combat counterfeit liquor sales, such as whisky by reading the tag on the bottle using the dongle, which transfers the unique verification number of each product to the server of the National Tax Service via wireless Internet [96]. Active RFID battery-powered tags are used by Beverage Metrics Company to provide a complete solution to track bottles of liquor. With this system, a bar's manager can measure how much liquor a bartender pours per drink, based on a tilt sensor in the RFID tag. In addition, customers can also use the system to receive an alert if a bottle of liquor or wine disappears from the system (and therefore may have been stolen) [97].

A great advance in the application of RFID has been the integration of time-temperature sensors to RFID devices which are attached to boxes or pallets during transport allowing tracking of food temperature during the whole food chain. This results in an improvement in supply chain management efficiency [8]. As an example, an advanced technology is applied to authenticate and track fine wines from producer to consumer, monitoring and recording the storage temperature by using eProvenance Fine Wine Cold Chain™ Systems which are a combination of semi-passive (battery assisted) and passive RFID tags [94].

Near field communication (NFC) is a form of data recognition technology that is commonly used for mobile phones, appearing, for example, in the now-familiar form of QR (quick response) codes. This technology is an upgrade to RFID technology which enables the exchange of data between devices at distances fewer than 10 cm [100]. This short-range communication technology has been applied in beverage packaging, such as wine and whisky, by Diageo Company with electronically tagged bottles providing supply-chain tracking to consumers [101]. The bottle uses NFC technology, integrated with labeling, to let consumers interact with the package using NFC-enabled smartphones. A thin, flexible NFC tag is attached to each bottle, enabling consumers to simply tap their phone to the bottle's back label to access product and brand information. Anti-counterfeiting is another strong potential market for printed electronic systems. NFC is particularly well positioned, as the protocol is increasingly becoming commonplace on smartphones, allowing modern consumers to carry out product verification themselves [102]. NFC can be seen as an evolution of RFID, both of them use radio frequencies for communication; however RFID can operate in a long distance range, therefore it is not suitable for exchanging sensitive information since it can be vulnerable for various kinds of attacks. Contrary NFC has a very short transmission range, in this way NFC-based transactions are inherently secure.

4. Closing Remarks

Several studies related to beverage packaging in different materials have been summarized; focusing the attention on the overall aroma profile evolution over time, chemical degradation processes, and molecular transfers (aroma or oxygen) through the bottle and the cap. The impact from

these effects plays an important role in the final beverage since these products could be rejected by consumers if these effects cannot be controlled by the producer.

However, different alternatives are emerging as a consequence of the growing demand of new packaging systems for minimally-processed foods, but it is critical and necessary that packaging formats that enable wider distribution of these products evolve. In this sense, new packaging technologies based on active and intelligent concepts will continue to evolve in order to increase the quality and shelf-life of beverage products.

Conflicts of Interest

The authors declare no conflict of interest.

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